Synthesis and X-ray Crystal Structure of the Heterobimetallic Complex $[(OC)_3Fe(\mu\text{-dppm})(\mu\text{-I})PtI]$

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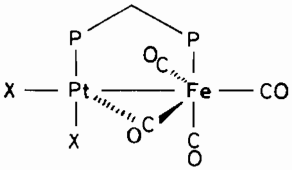
(Received July 15, 1986)

$Ph_2PCH_2PPh_2$ (dppm) has been used extensively over several years as a bridging ligand in bimetallic chemistry [1]. Recently, we reported that $[(OC)_4Fe(\text{dppm-}P)]$, acting as a bidentate chelate, would coordinate to Pt(II) in the complexes $[(OC)_3Fe(\mu\text{-dppm})(\mu\text{-CO})PtX_2]$ (1) X = Cl or Br [2]. An X-ray structural determination of **1**, X = Br, indicated the



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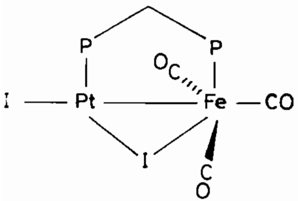
presence of a weakly semi-bridged carbonyl group, although we concluded that the metal–metal bonding was largely of the donor–acceptor type *viz.* Fe → Pt. We now report that our attempts to prepare the corresponding di-iodide gave a heterobimetallic with a different structure.

Treatment of $[(OC)_4Fe(\text{dppm-}P)]$ with $[PtI_2\text{-cyclo-acta-1,5-diene}]$ in dichloromethane gave $[(OC)_3Fe(\mu\text{-dppm})(\mu\text{-I})PtI]$ (**2**) in 68% isolated yield.



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2 was also prepared, quantitatively, by treating **1** (X = Br) with MeI in dichloromethane. **2** was characterized by elemental analysis and by ^1H and $^{31}p\{^1H\}$ NMR spectroscopy. The IR spectrum (dichloromethane solution) showed ν(CO) at 2040s and 1988s (broad) cm^{-1}, indicating the absence of a bridging carbonyl. The spectral parameters of **2** were sufficiently different from those of **1** (X = Cl or Br) to suggest a different structure: we have therefore determined the crystal structure of **2**, which is shown in Fig. 1; selected data are in the Figure caption. The Fe → Pt distance of 252.3(4) pm indicates a metal–metal bond and is close to those found in other crystallographically characterised compounds of these metals [3, 4]. The Fe → I distance, 261.1(4) pm and Pt → I distance, 266.4 pm suggest that the iodide ligand is almost symmetrically bridging the metal centres. The metal–metal bonding in **2** can be viewed as of the donor–acceptor type *viz.* Fe → Pt. In this way, the bridging iodide must contribute two electrons to each metal thus satisfying an 18e Fe(0) centre and a 16e Pt(II) centre. Alternatively, the molecule could be described as having a single metal–metal bond between d^7 Fe(I) and d^9 Pt(I) centres. The ν(CO) bands of **2** tend to support the Fe(0)–Pt(II) assignment as they are similar to those found in previously characterized Fe(0) compounds containing a $Fe(CO)_3$ fragment, e.g. $[Fe(CO)_3(\eta^4\text{-buta-1,3-diene})]$ $\nu(CO) = 2051$ and $1978\ cm^{-1}$ [5] and $[Fe(CO)_3(\eta^4\text{-cyclo-octa-1,3-diene})]$ $\nu(CO) = 2043$, 1974 and $1971\ cm^{-1}$ [6].

The structural differences between **1** and **2** can, in part, be rationalized in terms of the relative size of iodide and bromide ligands. A structure like **1**, with a *cis*-dihalide moiety, will be much more sterically strained in the case of iodide and this strain can be somewhat relieved by one of the iodide ligands adopting a bridging position, with displacement of CO, as in **2**. Also iodide is a better bridging group than bromide for soft metal centres.

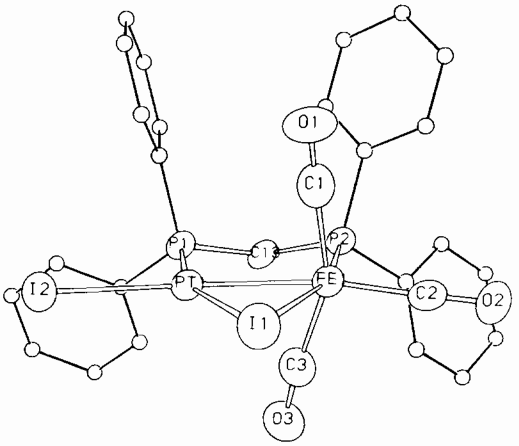

Fig. 1. Molecular structure of $[(OC)_3Fe(\mu\text{-dppm})(\mu\text{-I})PtI]$ (**2**). Selected interatomic distances: Fe–Pt 252.3(4), Fe–I(1) 261.6(4), Pt–I(1) 266.4, Pt–I(2) 265.6 pm. Selected angles: Pt–I(1)–Fe 57.1, I(1)–Pt–I(2) 102.7°.

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0020-1693/86/$3.50

Halo-bridged complexes of iron carbonyls are rare [7] and **2** appears to be the first example of an iron heterobimetallic containing a halide bridge. Its formation further illustrates the flexibility of dppm as a bridging ligand, in accommodating and stabilising unusual structural types.

Acknowledgements

We thank the S.E.R.C. and Johnson Matthey P.L.C. for support.

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